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Selected US specifications from IPC sub-classes C08F C09D

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(54) Treatment of surfaces and compositions for use therefor

(57) A method of treating a surface so as to inhibit the adhesion of living organism thereto comprises treating the surface with a composition comprising a polymer having defined repeating units comprising (A) hydrocarbyl groups with pendant acidic and/or basic groups and (B) pendant polyalkylene oxide groups (the acidic or basic groups being optional). The polymer compositions and the polymers themselves are also claimed. Typical polymers are copolymers of α-methoxy-ω-methacryloyloxy-polyethylene glycol with methacrylic acid, N-methacryloyl aniline or N-N-dimethyl-2-aminoethyl methacrylate.

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SPECIFICATION

Treatm nt of surfaces and compositions for use therefor

This invention relates to the treatment of surfaces so as to reduce th adhesi n of living organisms th reto and to compositions and polymers for use therefor.

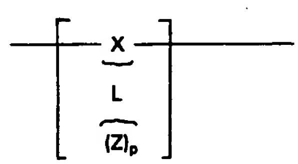
The probelms caused by the adhesion of living organisms to surfaces, especially to surfaces subjected to an aqueous environment, are well known. An example is the fouling of underwater surfaces in, for example, the sea, rivers, lakes, canals, swimming pools, industrial plant, pipes, etc. This fouling is caused by the attachment to those surfaces of a variety of micro and other organisms which then grow and multiply so as eventually to cause a significant problem in relation to the surface concerned. Thus, in the case of a ship's hull, the growth of marine organisms thereon increases the frictional resistance of the hull to passage through water and so increases fuel consumption and/or reduces the speed of the ship. Removal of the growths by cleaning and repainting the ship's hull in a dry dock is extremely expensive and time-consuming.

One approach to these problems has been to use biocides. Thus, it is known to apply to ships' hulls anti-fouling coatings in which the active ingredient is a biocide which is slowly released from the coating over a period in sufficient concentration to be lethal to marine organisms in the immediate vicinity of the protected surface. Eventually, the concentration of biocide in the coating falls below the lethal concentration and the coating must be renewed. For a time, this method provides an effective means of reducing surface fouling but, in addition to the need for renewal, a disadvantage of this technique is the danger to the marine environment posed by the continuous release of toxic materials such as organotin and copper compounds.

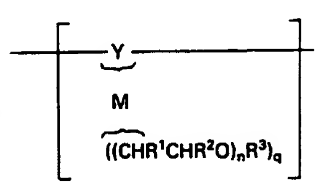
Another approach to this type of problem relies on the use of agents which are not toxic to the offending organisms but prevent or reduce their adhesion to the surface in question. An example of this approach in relation to the protection of ships' hulls is described in the Journal of Coatings Technology, *54*, silica-bearing methyl siloxane resin applied respectively to PVC and steel panels showed marine fouling resistance for a short period of time. According to the authors, no non-toxic anti-fouling coatings have reached a commercial stage.

A method of treating a rather different kind of marine substrate is described in Japanese Patent Publication No 52-81289 (81289/77) which is concerned with preventing the attachment of marine creatures to the surface of shellfish. The method comprises forming a water-swellable polymer on the surface of the shell by polymerising a monomer thereon in the presence of an acidic sulphite ion and a peroxide. This document specifically describes the formation of a water-swellable polymer on the shells of pearl oysters by the polymerisation of acrylamide together with a minor amont of methylene-bis-acrylamide. Other monomers mentioned include the polyethylene glycol and polypropylene glycol esters of acrylic and methacrylic acids, vinyl pyrrolidone, vinyl pyridine and styrene sulphonic acid. In order to the polymer to be strongly held to the surface of the shell, the use of the acidic sulphite ion is essential.

The present invention provides a method of treating a surface of an object so as to inhibit the adhesion of live organisms thereto which method, subject to a disclaimer defined hereinafter, comprises applying to the surface a composition comprising at least one polymer which polymer comprises one or more repeating units of general structure A



and one or more repeating units of general structure B



wherein X, which in the repeating units of structure A may be the same or different and Y, which in the repeating units of structure B may be the same or different, are hydrocarbyl residues or suitably substituted derivatives thereof;

Z, wh re present, which in th rep ating units of structure A may be the same or different, is a group bearing an acidic r basic substituent;

R^1, which in th same repeating unit of structure B (when n or q is two or more) or in different units of structure B may b the same r different is hydrogen or methyl;

R^2, which in the same repeating unit of structure B (wh n n or q is 2 r more) or in different units of structure B may be the same or different, is hydrogen or methyl; except that

R^1 and R^2 in a single unit (CHR^1CHR^2O) cannot both be methyl;

R^3, which in the same repeating unit of structure B (when q is 2 or more) or in different repeating units of structure B may be the same or different, is hydrogen or a lower alkyl group containing up to five carbon atoms, or an acyl group derived from an alkanoic acid having up to five carbon atoms;

n is a number between 1 and 60;

p is 0, or a number of from 1 to 4;

q is a number of from 1 to 4;

and wherein when p is not 0 each Z group is joined via an intermediary or intermediaries L to the hydrocarbyl residue X, and in cases where p is 2 to 4 may be joined by L to the same or different carbon atoms of X; and wherein L represents one or more intermediaries, and wherein L may be the same or different in the repeat units of structure A and is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a Z group with X, except that more than two Z groups cannot be directly linked to the same carbon atoms in X and in that L is absent when p is 0; and wherein each (CHR^1CHR^2O)n group is joined via an intermediary or intermediaries M to the hydrocarbyl residue Y, and in cases where q is 2 to 4 may be joined by M to the same or different carbon atoms of Y; and wherein M represents one or more intermediaries, and wherein M may be the same or different in the repeat units of structure B and is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a $(CHR^1CHR^2O)_n$ group with Y, except that more than two $(CHR^1CHR^2O)_n$ groups cannot be directly linked to the same carbon atom in Y;

There is further provided according to the invention a composition for use in treating a surface of an object so as to inhibit the adhesion of live organisms thereto, wherein, subject to a disclaimer defined hereinafter, said composition comprises at least one polymer comprising one or more repeating units of general structure A and one or more repeating units of structure B, where A and B are as defined hereinbefore.

Naturally the said polymer will be dispersed or dissolved in a suitable medium, vehicle or carrier therefor in the composition, which will often comprise mainly water, i.e. be aqueous based. However, the medium or carrier could also be organic based (e.g. ethanol or ethanol/water based) or even the matrix of a polymer. Other ingredients as required may also of course be included in the composition.

There is further provided according to the invention a polymer for use in the treatment of surface of an object so as to inhibit the adhesion of live organisms thereto, which polymer, subject to a disclaimer defined hereinafter, comprises one or more units of general structure A and one or more units of structure B, where A and B are as defined hereinbefore.

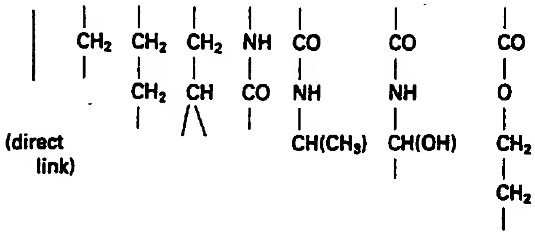
Where the surface which is to be treated is a hydrophobic surface, for example, a plastics material, e.g. polystyrene, it is often preferred that p is 0 (so that L is absent), i.e. there are no substituents Z on the polymer backbone. In such cases it is often convenient that X bears a lower alkyl group, e.g. methyl, and/or a polar group, e.g. $-CO_2R^4$ where R^4 is a lower alkyl group.

Where present, all the groups Z may be acidic or all the groups Z may be basic or a proportion of the groups Z may be basic and a proportion may be acidic, e.g. an amphoteric polymer may be obtained.

Examples of acidic groups that Z can represent (where present) are carboxylic acid groups, phosphates, sulphates, and phosphonates. Examples of basic groups which Z may represent include primary, secondary and tertiary amino groups, and quaternary ammonium groups.

In structure A, each Z group (where present) is joined to the hydrocarbyl residue X by means of an intermediary or intermediaries (i.e. by a linking entity or entities), this or these being denoted by L, which (if present, i.e. p not being 0) is selected from one or more direct links (i.e. one or more direct bonds) and one or more groups of atoms each group providing a chain of one or more atoms for linking a Z group with X. In cases where p is 2 to 4, each Z group may be joined by L to the same or, in cases where L represents more than one intermediary, to the same or different carbon atoms in X, although more than two Z groups cannot of course be directly linked to the same carbon atom of X (and also assuming that in such cases X has at least 2 carbon atoms, whereas it should be appreciated that it is within the scope of the invention for X to have only 1 carbon atom). It will be noted that in principle L can represent up to 4 separate intermediaries in structure A (in cases where p is 4). L may be the same or different in the repeat units of structure A.

In cases where L represents one or more groups of atoms each group providing a linking chain of atoms, the chain will normally comprise one or more carbon atoms (which could e.g. include carbon atoms in an aryl ring) and/or hetero atoms (particularly N and/or O). Examples of possible linkages provided by L are:

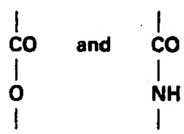


where (apart from the direct link) the top link is to X and the bottom link(s) is to Z.

It may be advantageous (e.g. when treating non-hydrophic surfaces) in structure A that p is 1 or 2 (so that L can then represent one, or at most two intermediaries).

In structure B, each $(CHR^1CHR^2O)_n$ group is joined to the hydrocarbyl residue Y by means of an intermediary or intermediaries (i.e. by a linking entity or entities), this or these being denoted by M, which is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a $(CHR^1CHR^2O)_n$ group(s) with Y. In cases where q is 2 to 4, each $(CHR^1CHR^2O)_n$ group may be joined by M to the same or, in cases where M represents more than one intermediary, to the same or different carbon atoms in Y, although more than two $(CHR^1CHR^2O)_n$ groups cannot of course be directly linked to the same carbon atom of Y (and also assuming that in such cases Y has at least 2 carbon atoms, whereas it should be appreciated that it is within the scope of the invention for Y to have only 1 carbon atom). It will be noted that in principle M can represent up to 4 separate intermediaries in structure B (in cases where q is 4). M may be the same or different in the repeat units of structure B.

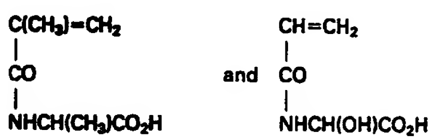
While M may represent one or more direct links, it is preferred in the present invention that M is one or more groups of atoms each group providing a linking chain of atoms; such a chain will normally comprise one or more carbon and/or hetero atoms (particularly N and/or 0). Particularly preferred examples of linkages provided by M are:



where the top link is to Y and the bottom link is to $(CHR^1CHR^2O)_n$.

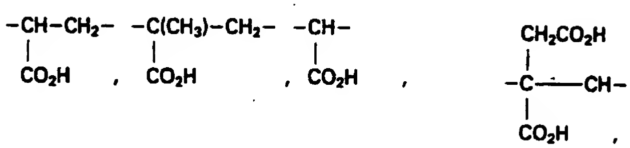
It is preferred in structure B that q is 1 or 2 (so that M can then represent one, or at most two intermediaries).

Preferably the structure A represents the repeating unit derived from the polymerisation (usually free-radical initiated) of one or more polymerisable olefinically unsaturated monomers which bear a basic group, e.g. a tertiary amino group, or an acidic group, e.g. a carboxylic acid group. Examples of such carboxylic acid group-bearing monomers are acrylic acid, methacrylic acid, maleic (or fumaric) acid, itaconic acid and the acids of formulae



N-methacryloyl alanine   N-acryloyl hydroxy glycine

respectively giving rise to the following structures for A.



```
-C(CH3)-CH2-              -CH-CH2-
 |                          |
 CO              and        CO
 |                          |
 NHCH(CH3)CO2H              NHCH(OH)CO2H
```

An example of a tertiary amino-bearing unsaturated monomer is N,N-dimethyl-2-aminoethyl methacrylate, $CH_2=C(CH_3)COOCH_2CH_2N(CH_3)_2$, giving rise to the repeating unit structure for A:

```
 CH3
 |
-CH-CH2-
 |
 CO       CH3
 |       /
 OCH2CH2N
         \
          CH3
```

Preferred monomers for yielding units of structure A at out present stage of development are methacrylic acid, maleic acid, and N,N-dimethyl-2-aminoethyl methacrylate. Often, the repeating units A will all be of the same specific structure, although the scope of the invention is intended to embrace polymers having repeating units A of more than one specific structure (e.g. 2 or 3 different specific structures).

Preferably the structure B represents the repeating unit derived from the polymerisation (usually free-radical initiated) of a polymerisable olefinically unsaturated ester or amide formed from the reaction of an unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof such as an acid chloride or anhydride) and a hydroxy compound of formula

$$HO\!\leftarrow\! CHR^1CHR^2O)_nR^3$$

(to form the ester) or an amine of formula

$$H_2N\!\leftarrow\! CHR^1CHR^2O)_nR^3$$

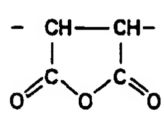
(to form the amide). Preferably the acid used is acrylic or methacrylic acid, particularly the latter, giving rise, respectively, to the following structures for B:

```
-C(CH3)-CH2-                       -C(CH3)-CH2-
 |                                  |
 CO                     and         CO
 |                                  |
 O⟵CHR¹CHR²O)n R³,                  NH⟵CHR¹CHR²O)n R³
```

Normally the repeat units B will all be of the same specific structure, although the scope of the invention is intended to embrace polymers having repeat units B of more than one specific structure (e.g. 2 or 3 different specific structures).

The repeating units of structure B may alternatively be formed by the partial esterification or amidification of an already-polymerised olefinically unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof such as an acid chloride or anhydride) using, preferably, an alcohol of formula $HO\!\leftarrow\! CHR^1CHR^2O)_nR^3$ or an amine of formula $H_2N\!\leftarrow\! CHR^1CHR^2)_nR^3$. The remaining (unesterified or unamidified) carboxyl groups with their associated sections of the polymer backbone will of course provide acidic units of structure A (it may of course be necessary to hydrolyse residual acid-derivative groups back to carboxyl when an acid derivative is used).

In one interesting aspect of this alternative method for producing units of structures A (Z being carboxyl) and B, an olefinically unsaturated cyclic anhydride may be used to produce both the acid and ester/amide groups of the resulting polymer. For example, maleic anhydride may be polymerised to form a polymer of repeat unit



and the resulting repeating units A and B after esterification with $HO\!\leftarrow\! CHR^1CHR^2O)_n R^3$ or amidification with $H_2N\!\leftarrow\! CHR^1CHR^2O)_n R^3$ will be

A

or

B

(if esterification) (if amidification)

It is thus apparent that there are two preferred processes for preparing polymers according to the invention.

The first process (a) comprises polymerising (usually by free-radical initiation) an olefinically unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof) and partially esterifying or amidifying the resulting polyacid (or derivative thereof) with at least one alcohol of formula $HO(CHR^1CHR^2O)_n R^3$ or at least one amine of formula $H_2N(CHR^1CHR^2O)_n R^3$.

The second (and generally more preferred) process (b) comprises copolymerising (usually by free-radical initiation) at least one polymerisable ester or amide, formed from the reaction of a first olefinically unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof) and an alcohol of formula $HO\!\leftarrow\! CHR^1CHR^2O)_nR^3$ or an amine of formula $H_2N\!\leftarrow\! CHR^1CHR^2)_nR^3$, with at least one second olefinically unsaturated carboxylic acid and/or with at least one olefinically unsaturated tertiary amino compound.

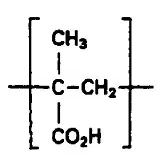
Both processes will yield repeat units of structure A and structure B as hereinbefore defined.

In the polymers of the invention, it is preferable that substantially all the R^1 and R^2 groups are hydrogen so that $(CHR^1CHR^2O)_n$ is $(CH_2CH_2O)_n$. Such groups may be derived from the alcohol $HO\!\leftarrow\! CH_2CH_2O)_n R^3$ or the corresponding amine $H_2N\!\leftarrow\! CH_2CH_2O)_n R^3$. Where a proportion of the R^1 and R^2 groups in the polymer are methyl, all the R^1 or R^2 groups in one or more of the $(CHR^1CHR^2O)_n$ chains may be methyl or one or more (but not all) of the R^1 or R^2 groups in one or more of the $(CHR^1CHR^2O)_n$ chains may be methyl. R^1 and R^2 cannot, however, both be methyl in the same unit (CHR^1CHR^2O) as specified hereinbefore. Such a chain could for example be derived from an amine such as $H_2N\!\leftarrow\! CH(CH_3)CH_2O)_2(CH_2CH_2O)_4C_4H_9$ (where CHR^1CHR^2 is $CH(CH_3)CH_2O$ and CH_2CH_2O, n is 6, and C_4H_9 is normal butyl), or other analogous amines (varying CHR^1CHR^2O and$_n$). It could also be derived from an alcohol, such as $HOCH(CH_3)CH_2OH$

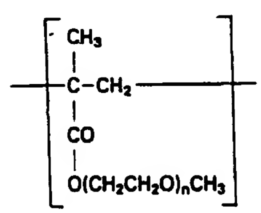
Preferably R^3 is a lower alkyl group containing up to 5 carbon atoms, e.g. n-butyl or (more preferably) methyl. It may, nevertheless, be hydrogen.

Specific examples of polymers that we have prepared and investigated have repeating units structures A and B as follows:

A

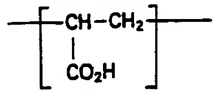
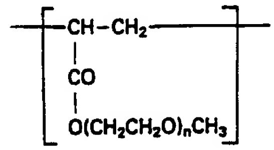


B

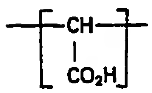
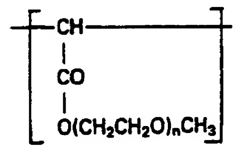


(n = 3,6,8,23,45)

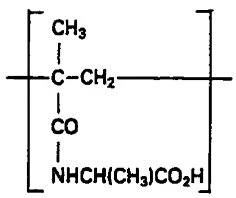
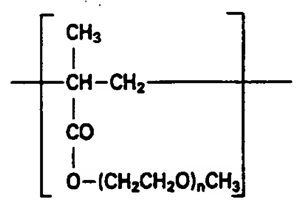
A B

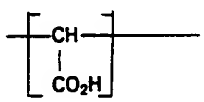
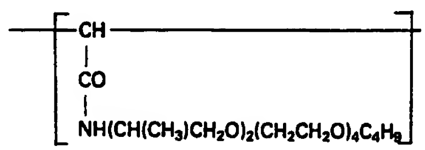
(n = 8)

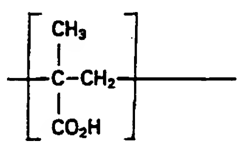
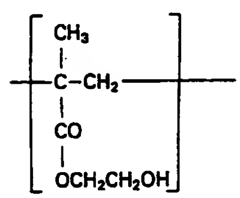
(n = 6)

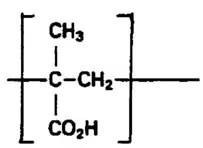
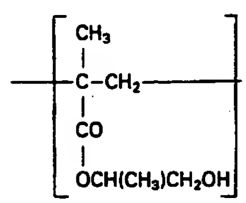
(n = 8)

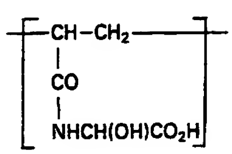
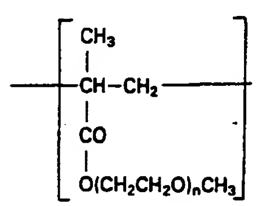
(n = 6)

(n = 1)

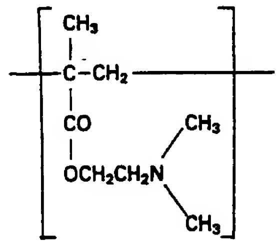



(n = 1)

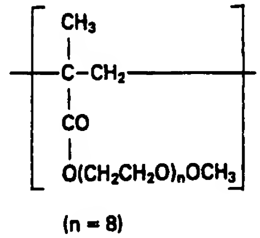



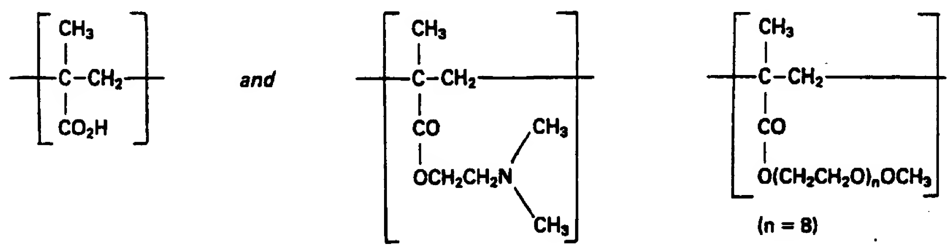
(n = 8)

A



B





In the polymers of the invention, n is a number of from 1 to 60 as defined herein. Often, however, n is preferably from 1 to 20.

The ratio of Z groups to $-CHR^1CHR^2O-$ groups (assuming Z is present) is preferably within the range of from 1:20 to 20:1 and more preferably the ratio is from 1:5 to 5:1.

It is to be understood that the definition of the polymer contained in the method of the invention (as given hereinbefore) is also intended to embrace a polymer in which at least some of the acidic or basic Z groups in the repeat units of structure A have been converted to the corresponding salt anions or cations, e.g. CO_2^- in the case of CO_2H groups or quaternary ammonium cations in the case of amines (these still being considered as carboxyl or amino groups as far as the defintion of A is concerned). Such a conversion could e.g. be effected as a resulting of incorporating the polymer into an alkaline or acidic medium (respectively).

Typically the polymers of the invention have molecular weights within the range of from 5000 to 500,000, although we do not exclude the possibility that suitable polymers having molecular weights outside this range may be used in the present invention.

The groups X and Y may be unsubstituted hydrocarbyl radicals or may be substituted with groups such as hydroxy, alkoxy and halogen (e.g. chlorine) provided the desired properties of the polymers are not adversely affected. Preferably however, the groups X and Y are unsubstituted, i.e. have only groups linked by L and M attached to them.

The polymers of the invention may also contain up to 50% w/w (i.e. 0 to 50% w/w), sometimes up to 10% w/w (i.e. 0 to 10% w/w), of repeating units other than those of structures A and B, which form the backbone thereof, and these may provide one or more in-chain or pendant hetero atoms (per unit). Such repeating units must not of course adversely affect the properties of the resulting antifouling compositions. More usually however, the polymers of the invention have substantially all their repeating units with structures A and B.

The method of the invention is applicable to any object of which a surface may be subjected to infestation with adherent live organisms which may be micro-organisms such as bacteria and algae or larger organisms including marine creatures such as barnacles.

Particularly, but not exclusively, the invention is applicable to solid objects, for example, vessels, pipes and machinery of all types, e.g. cooling towers, stills, and paper mills, which have one or more surfaces in contact with an aqueous medium containing live organisms. The invention is especially applicable to the hulls of ships and boats and to other structures having a marine environment. Moreover, the object which is treated in accordance with the invention may be a solid coating, for example a paint coating which has been applied to a substrate for protective or decorative purposes and which, itself, requires, protection from adhesive organisms. In some cases the composition may be part of a surface coating formulation which is to be applied to a surface so that the surface coating formulation serves as a vehicle for the composition.

Surfaces which may be treated in accordance with the invention include the surfaces of inorganic materials such as metals, glass or silica and organic materials such as plastics articles and other polymeric materials such as the aforementioned coatings.

The most suitable method of applying the composition to the surface depends upon the particular composition and surface involved and also upon the situation in which infestation occurs. The simplest

method, applicable to closed aqueous systems rather than to a marine environment, is merely t add the composition to an aqueous medium in contact with a surface and allow the compound to be absorbed by th surface. This method is useful for the protection of plastics surfaces including coatings such as paint films. In some cases, however, it is necessary to treat a surface before it is brought into contact with an aqueous medium, for example by treating the surface with a relatively concentrated soluti n f th compositi n, so that the polymer is absorbed on or reacts with the surface. Thus, a metal surface would normally be treated in this way. A further method of applying the polymer to a surface is to incorporate it into the material having said surface. This method is also applicable to the protection of polymeric materials such as plastics articles and paint films. Incorporation of the polymer into the polymeric material can be either physical or chemical. In the latter case, the polymer should have a group which reacts with substituents in the polymeric material.

The effectiveness of the treatment provided by the method of the invention decreases with the passage of time at a rate depending upon the mode of attachment between the polymer and the surface and the nature of the environment. When the point is reached that the treatment has ceased to provide significant protection against infestation, the surface will normally be subjected to re-treatment.

In addition to the specific applications mentioned above, the method of the invention may be used for the protection of other surfaces on which microbial adhesion may occur. Examples of such surfaces include the internal parts of dialysis machines and artificial organs. The invention may also be used to protect surfaces from airborne micro-organisms, for example bacteria and fungal spores.

In our copending European application of even date, which claims priority from GB application No 84 28523, the latter having the same filing date as GB Application No 84 28524 from which the present application claims priority, there is claimed an oral hygiene composition which is effective for preventing the adherent deposition of cariogenic or other oral bacteria on mammalian (human) teeth and which comprises polymeric material falling within the scope of the polymer definition for polymers used in the method of the present invention. This oral hygiene composition comprises an effective amount of at least one polymer in a pharmaceutically acceptically vehicle therefor, which polymer comprises one or more repeating units of a general structure which is identical in scope with the structure B of the present invention, and also one or more repeating units of another general structure which is the same in scope as the structure A of the present invention, except that in these repeating units of our copending application, Z represent only CO_2H and p must not be O. There is also claimed in this copending European application the polymers per se which can be used in the oral hygiene compositions, and a process for making such polymers, and a process for treating teeth with the claimed composition. We wish to disclaim any method of treatment according to the present invention where such method is to the treatment of mammalian (human) teeth. We also disclaim amy composition according to the present invention which could be used as an oral hygiene composition. We also disclaim any claim to a polymer per se which is used in the present invention and which falls with the scope of the polymers claimed in our said copending European application.

The present invention is now illustrated by the following examples. The prefix C before a number represents an example performed for comparative purposes

Examples 1 to 6

Examples 1 to 6 illustrate polymers (and their preparation) which may be used in the method of treatment according to the present invention. It was found that comonomers providing units A and B reacted so as to give polymers in which the mole ratio of A to B units therein was close to the mole ratio used for the starting monomers (indicating approximately equal reactivities), so that the latter ratio could be used for calculating the former, which was also checked in most cases using ordinary analytical techniques (chemical analysis, NMR, and acid-base titrations).

A typical polymer preparation, specifically applicable to the polymers of Examples 1 and 6 is now described. (Dry chemicals and solvents were used).

Methacryloyl chloride (0.11 moles) was added slowly with stirring to a slight molar excess of a 30% solution of 2,6-lutidine in toluene. Fuming occurred and a white precipitate formed. The mixture was cooled in an ice-bath and methoxy-ended polyethylene glycol (0.10 moles) was added dropwise over 3 hours with stirring under nitrogen. A copious white precipitate formed and stirring was continued for a further 2 hours. The reaction mixture was allowed to warm to room temperature. The precipitate was filtered off and washed with small volumes of toluene. The combined filtrates were evaporated to dryness (over 90% yield) on a rotary evaporator at 45°C. The structure of the product was confirmed, by IR, NMR and vinyl bond titration, as substantially α-methoxy-ω-methacryloyloxy-polyethylene glycol.

The monomers methacrylic acid and α-methoxy-ω methacryloyloxy-polyethylene glycol, in selected molar ratios (total 25 grams), and solvent (usually ethanol or ethanol/water mixture) (300 mls) were charged to a reaction vessel at 70°C. Initiator (1.8×10^{-3} moles) in solvent (20 mls) was added and the reaction mixture was stirred (200 rpm) at 70°C for 24 hours. Further initiator (7×10^{-4} moles) in solvent (20 mls) was added and the reaction was continued for a further 24 hours. The reaction mixture was evaporated on a rotary evaporator under reduced pressure to leave a copolymer (usually about 95% yield). The compositions of the copolymers are given in Table 1, which also gives the values for n and the ratio of Z to (CHR^1CHR^2O) groups.

Substantially th same sort f technique was employed for the preparation of the polymers of Examples 2, 3, 4, and 5, except that:

– f r the pr paration of the polym r of Example 4, N-methacryloyl alanine i.e. $CH_2{=}CH(CH_3)CONH$-

$(CH_3)CO_2H$, prepared by reacting the Na salt of alanine with methacryloyl chlorid , was used in place of methacrylic acid for the polymerisation

– f r the preparation of the polymer of Example 5, N,N-dimethyl-2 aminoethyl methacrylate (DMAEM) was used in place of methacryli acid for th polymerisation

– for th preparation of the polymers of Examples 2 and 3, there was used a mixture of methacrylic acid and DMAEM (molar ratios 1.8:1 in Example 2 and 1:1 in Example 3) in place of methacrylic acid on its own.

The compositions of these polymers are also given in Table 1.

The polymers of Examples C7, C8, and C9 were prepared for comparative purposes, their compositions being given in Table 1.

It will be noted that the polymer of Example 5 is a polymer as claimed in the present invention, whereas the polymers of Examples 1, 2, 3, 4 and 6, although usable for the method of treatment according to the present invention, cannot themselves be claimed per se since they fall within the scope of the polymers claimed in our copending European application discussed hereinbefore, which comprise "A" repeating units (in which Z is CO_2H) and can include 0 to 50 wt % of units other than A or B (as defined in that specification).

TABLE 1

Ex. No.	*Repeating Units Type A*	*Type B*	*Value of n*	*Molar ratio of A:B*	*Ratio of Z: (CHR^1CHR^2O) groups (approx.)*
1	MA	PEG350MAt	8	3:1	1:2.7
2	MA and DMAEM	PEG350MAt	8	2.7:1	1:3
3	MA and DMAEM	PEG350MAt	8	3:1	1.2.7
4	MAlAt	PEG350MAt	8	3:1	1.2.7
5	DMAEM	PEG350MAt	8	3:1	1.2.7
6	MA	PEG350MAt	8	6:1	1:1.3
C7	Poly DMAEM				
C8	Polyacrylic acid				
C9	Polymethacrylic acid				

Abbreviation Code for Table 1

MA: units derived from methacrylic acid

PEG350MAt: units derived from polyethylene glycol (PEG) capped with a methoxy and a methacryloyl group, i.e. from $CH_2{=}C(CH_3)COO(CH_2CH_2O)_nCH_3$ where the molecular wt of the polyethylene glycol (PEG) portion thereof is 350 (n = 8)

DMAEM: units derived from N,N-dimethyl-2-aminoethyl methacrylate

MAtAl: units derived from N-methacryloyl alanine, i.e. from $CH_2{=}CH(CH_3)CONHCH(CH_3)CO_2H$

Examples 10 to 14 and C15 to C17

These examples illustrate the extent of the reduction in microorganism adhesion obtained using the method of treatment according to the invention.

Clean glass slides were used to provide model substrate surfaces. *Streptococcus mutans* NCTC 10449 and *Serratia marcescens* were used as the standard organisms.

The aforementioned slides were held in a 1% w/v aqueous (or alcoholic) solution of the polymers in a petri-dish for 5 minutes at ambient temperature and were then washed by shaking 5 times in a container of flowing water ("treated slides").

S.mutans were grown at 37°C in a Brain/Heart Infusion growth medium, and *S.marcescens* were grown at ambient temperature in Nutrient Broth growth medium. A portion (20 mls) of the culture at a concentration of 10^9 cells/ml was centrifuged at 4,000 rpm f r 10 minutes and th cells were resusp nded in modified Ringer's salts s lution (0.54 grams p r litre NaCl; 0.02 grams per litre KCl; 0.03 grams per litre $CaCl_2$; and 0.75 grams per litr sodium mercapt ac tate), recentrifuged, resuspended and dilut d 10× in Ringer's salts

solution. The S.marcescens culture was diluted 10× in distilled water.

The treated slides were immersed in the aforementioned suspensions for 2 h urs. The treated slides were then washed by shaking 5 times in a container of flowing water and rganisms adhering theret were stained using Loeffler's Methylene Blu (30 ml of 95% ethanol, 0.3 gram methylene blu and 100 ml of water). Microscopic examinati n was used to estimate the reduction in bacterial adhesi n of th clean slides versus untreated control slides. The results are given in Table 2.

TABLE 2

Ex. No.	*Polymer from Ex.No.*	*% Reduction compared to untreated control slide* S.mutans	S.marcescens
10	1	95	85
11	2	94	98
12	3	96	95
13	4	93	96
14	5	a	97
C15	C7	0	72
C16	C8	30	0
C17	C9	25	0

a: not determined.

Examples 18 to 21

The polymer of Example 3 was tested for its effectiveness in preventing the adherent deposition of a range of microorganisms other than S.mutans and S.marcescens, the evaluation procedure being otherwise similar to that in Examples 10 to 14. The results are given in Table 3.

TABLE 3

Ex. No.	*Microorganism*	*% Reduction compared with untreated control*
18	Pseudomonas aeruginosa NCIB 10421	97
19	Bacillus subtilis NCIB 1650	95
20	Staphylococcus aureus NCIB 9518	99
21	Pseudomonas fluorescens NCIB 9046	93

Examples 22 to 25

The polymers of Examples 1, 4, and 6 were treated for their effectiveness in preventing the adhesion of *S.mutans* and *B.subtilis* NCIB 1650 microorganisms to stainless steel samples instead of glass, the evaluation procedure being otherwise the same as in Examples 10 to 14. The results are shown in Table 4.

TABLE 4

Ex. No.	*Polymer from Ex.No.*	*Microorganism*	*% Reduction compared to untreated control*
22	4	S.mutans	93
23	4	B.subtilis	96
24	1	S:mutans	93
25	6	B.subtilis	96

Examples 26 to 30

These examples employed a 2 hour "Universal Bottle Adhesion" test using samples of nylon fabric to pr vide the treated substrate under examination.

Small squares of fabric material were mounted on SEM (Scanning Electron Microscope) stubs using doubl sided sellotape. 1% solutions of polymers (from Examples 6, 3, and 4) were used to coat the fabric (Banlon N221 – nylon) by placing the stub plus fabric in the solution on a roller for 10 mins. The treated fabric was washed with 5 × 30 ml portions of distilled water in Universal plastic bottles. The stubs were then placed in 20 ml of microorganism suspension (overnight culture diluted × 10) in Universal bottles for 2 hours at room temperature. After 2 hours the microorganism suspensions were removed, the fabrics washed with a further 5 × 30 ml of water, fixed in a 2% glutaraldehyde solution, dried and observed under SEM in order to estimate the % reduction in adhesion levels compared to untreated controls. The results are shown in Table 5.

TABLE 5

Ex. No.	*Polymer from Ex.No.*	*Microorganism*	*% Reduction compared to untreated control*
26	6	S.mutans	95-99
27	3	S.mutans	95-99
28	4	S.mutans	95-99
29	6	S.marcescens	95-99
30	4	S.marcescens	95-99

Example 31

In this experiment, the polymer of Example 6 was incorporated into a film derived from a commercially available aqueous-based vinyl-acrylic polymer latex, 'Haloflex' 202 (Imperial chemical Industries PLC; the word 'Haloflex' is a registered trade mark), known to provide rust-protective film-coatings when applied to ferrous metal substrates.

20 g of the polymer of Example 6 were dissolved in 50 ml of industrial methylated spirits (IMS). This solution was slowly added to 134 g of 'Haloflex' 202 latex suspension with vigorous stirring. A control latex was prepared by adding 50 mls of IMS to 134 g of the polymer latex.

Films were cast on glass plates, and left to dry for several weeks. 2.5 cm discs were cut from the cast films, and used in 2 hour petri-dish adhesion experiments with S.mutans (as per the procedure of Examples 10 to 14). Numbers of bacteria adhered to the surface were determined using a bioluminescence technique (which measures only living bacteria) and microscopy.

The results are shown in Table 6.

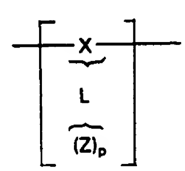
TABLE 6

% Reductions compared to Untreated Control	
Bioluminescence	Microscopy
99%	96%

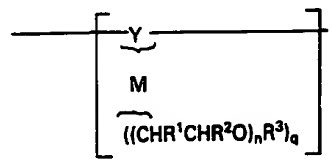
Subject to the foregoing disclaimers, what we claim is:

CLAIMS

1. A method of treating a surface of an object so as to inhibit the adhesion of live organisms thereto, which method comprises applying to the surface a composition comprising at least one polymer which polymer comprises one or more repeating units of general structure A



and one r more repeating units of general structure B



wherein X, which in the repeating units of structure A may be the same or different and Y, which in the repeating units of structure B may be the same or different, are hydrocarbyl residues or suitably substituted derivatives thereof;

Z, where present, which in the repeating units of structure A may be the same or different, is a group bearing an acidic or basic substituent;

R^1, which in the same repeating unit of structure B (when n or q is two or more) or in different units of structure B may be the same or different, is hydrogen or methyl;

R^2, which in the same repeating unit of structure B (when n or q is 2 or more) or in different units of structure B may be the same or different, is hydrogen or methyl;

except that R^1 and R^2 in a single unit (CHR^1CHR^2O) cannot both be methyl;

R^3, which in the same repeating unit of structure B (when q is 2 or more) or in different repeating units of structure B may be the same or different, is hydrogen or a lower alkyl group containing up to five carbon atoms, or an acyl group derived from an alkanoic acid having up to five carbon atoms;

n is a number between 1 and 60;

p is 0, or a number of from 1 to 4;

q is a number of from 1 to 4;

and wherein when p is not O each Z group is joined via an intermediary or intermediaries L to the hydrocarbyl residue X, and in cases where p is 2 to 4 may be joined by L to the same or different carbon atoms of X; and wherein L represents one or more intermediaries, and wherein L may be the same or different in the repeat units of structure A and is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a Z group with X, except that more than two Z groups cannot be directly linked to the same carbon atom in X and in that L is absent when p is 0; and wherein each $(CHR^1CHR^2O)_n$ group is joined via an intermediary or intermediaries M to the hydrocarbyl residue Y, and in cases were q is 2 to 4 may be joined by M to the same or different carbon atoms of Y; and wherein M represents one or more intermediaries, and wherein M may be the same or different in the repeat units of structure B and is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a $(CHR^1CHR^2O)_n$ group with Y, except that more than two $(CHR^1CHR^2O)_n$ groups cannot be directly linked to the same carbon atom in Y;

2. A method according to Claim 1 wherein p is 0, or is 1 or 2.

3. A method according to either Claim 1 or Claim 2 wherein M is one or more groups of atoms each group providing a linking chain of atoms.

4. A method according to any one of the preceding claims wherein q is 1 or 2.

5. A method according to any one of the preceding claims wherein the structure A represents the repeat unit derived from the polymerisation of one or more polymerisable olefinically unsaturated monomers which bear a basic group or an acidic group.

6. A method according to Claim 5 wherein the acidic group is a carboxyl group.

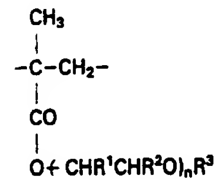
7. A method according to Claim 6 wherein structure A is derived from the polymerisation of one or more of acrylic acid, methacrylic acid, maleic acid, itaconic acid, N-methacryloyl alanine and N-acryloyl hydroxy glycine.

8. A method according to any one of Claims 5 to 7 wherein the basic group is an amino group.

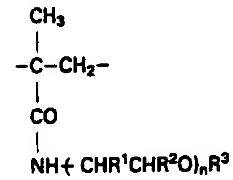
9. A method according to Claim 8 wherein structure A is derived from the polymerisation of N,N-dimethyl-2-aminoethyl methacrylate.

10. A method according to any one of the preceding claims wherein structure B is the repeat unit derived from the polymerisation of a polymerisable olefinically unsaturated ester or amide formed from an olefinically unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof) and a hydroxy compound of formula $HO-(CHR^1CHR^2O)_nR^3$ (to form the ester) or an amine of formula $H_2N\!-\!(CHR^1CHR^2O)_nR^3$ (to form the amide).

11. A composition according to Claim 10 wherein the acid used for the ester or amide formation is methacrylic acid, and the corresponding structures B are respectively:



and



12. A method according to any one of the preceding claims wherein the ratio of the number of Z groups to the number of (CHR^1CHR^2O) groups is from 1:20 to 20:1.

13. A method according to any one of the preceding claims wherein n is 1 to 20.

14. A method according to any one of the preceding claims where the said at least one polymer used has a weight average molecular weight of from 5000 to 500,000.

15. A method according to any one of the preceding claims wherein said composition is applied to a surface which is or will become in contact with an aqueous medium containing live organisms.

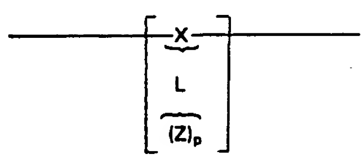
16. A method according to Claim 15 wherein the aqueous medium is provided by a marine, medical or industrial environment.

17. A method according to any one of the preceding claims wherein the surface to which the composition is applied is a solid coating such as a dry paint coating.

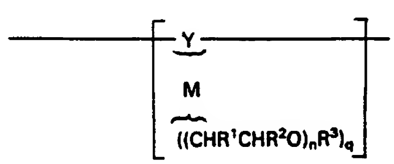
18. A method according to any one of the preceding claims wherein said composition comprises said polymer dispersed or dissolved in an aqueous or an organic-based medium, carrier, or vehicle.

19. A method according to any one of Claims 1 to 17 wherein said composition comprises said polymer dispersed in a solid polymeric matrix.

20. A composition having utility in the treatment of a surface of an object so as to inhibit the adhesion of live organisms thereto, which composition comprises at least one polymer which polymer comprises one or more repeating units of general structure A



and one or more repeating units of general structure B



wherein X, which in the repeating units of structure A may be the same or different and Y, which in the repeating units of structure B may be the same or different, are hydrocarbyl residues or suitably substituted derivatives thereof;

Z, where present, which in th r p ating units f structure A may be the sam or different, is a gr up bearing an acidic or basic substituent;

R^1, which in the same repeating unit of structure B (when n or q is two or more) r in different units of structure B may be the same or different is hydrogen or methyl;

R^2, which in the same repeating unit of structure B (when n or q is 2 or m re) or in different units of structure B may be th same r different, is hydrogen or methyl; except that

R^1 and R^2 in a single unit (CHR^1CHR^2O) cannot both be methyl;

R^3, which in the same repeating unit of structure B (when q is 2 or more) or in different repeating units of structure B may be the same or different, is hydrogen or a lower alkyl group containing up to five carbon atoms, or an acyl group derived from an alkanoic acid having up to five carbon atoms;

n is a number between 1 to 60;

p is 0, or a number of from 1 to 4;

q is a number of from 1 to 4; and wherein when p is not 0 each Z group is joined via an intermediary or intermediaries L to the hydrocarbyl residue X, and in cases where p is 2 to 4 may be joined by L to the same or different carbon atoms of X; and wherein L represents one or more intermediaries, and wherein L may be the same or different in the repeat units of structure A and is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a Z group with X, except that more than two Z groups cannot be directly linked to the same carbon atoms in X and in that L is absent when p is 0; and wherein each $(CHR^1CHR^2O)_n$ group is joined via an intermediary or intermediaries M to the hydrocarbyl residue Y, and in cases where q is 2 to 4 may be joined by M to the same or different carbon atoms of Y; and wherein M represents one or more intermediaries, and wherein M may be the same or different in the repeat units of structure B and is selected from one or more direct links and one or more groups of atoms each group providing a chain of one or more atoms for linking a $(CHR^1CHR^2O)_n$ group with Y, except that more than two $(CHR^1CHR^2O)_n$ groups cannot be directly linked to the same carbon atom in Y.

21. A composition according to Claim 20 wherein p is 0, or is 1 or 2.

22. A composition according to either Claim 20 or Claim 21 wherein M is one or more groups of atoms each group providing a linking chaim of atoms.

23. A composition according to any one of Claims 20 to 22 wherein q is 1 or 2.

24. A composition according to any one of the preceding Claims 20 to 23 wherein the structure A represents the repeat unit derived from the polymerisation of one or more polymerisable olefinically unsaturated monomers which bear a basic group or an acidic group.

25. A composition according to Claim 24 wherein the acidic group is a carboxyl group.

26. A composition according to Claim 25 wherein structure A is derived from the polymerisation of one or more of acrylic acid, methacrylic acid, maleic acid, itaconic acid, N-methacryloyl alanine and N-acryloyl hydroxy glycine.

27. A composition according to any one of Claims 20 to 26 wherein the basic group is a tertiary amino group.

28. A composition according to Claim 26 wherein structure A is derived from the polymerisation of N,N-dimethyl-2-aminoethyl methacrylate.

29. A composition according to any one of Claims 20 to 28 wherein structure B is the repeating unit derived from the polymerisation of a polymerisable olefinically unsaturated ester or amide formed from an olefinically unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof) and a hydroxy compound of formula $HO\text{+}CHR^1CHR^2O)_nR^3$ (to form the ester) or an amine of formula $H_2N\text{+}CHR^1CHR^2O)_nR^3$ (to form the amide).

30. A composition according to Claim 29 wherein the acid used for the ester or amide formation is methacrylic acid, and the corresponding structures B are respectively:

```
  CH3
  |
-C-CH2-
  |
  CO
  |
  O+ CHR1CHR2O)nR3
```

and

```
  CH3
  |
-C-CH2-
  |
  CO
  |
  NH+ CHR1CHR2O)nR3)
```

31. A comp sition according to any one of Claims 20 to 30 wherein the ratio of the number of Z groups (when present) to th number of (CHR^1CHR^2O) groups is from 1:20 to 20:1.

32. A m thod according to any one of Claims 20 to 31 wherein n is 1 to 20.

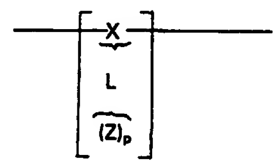
33. A composition according to any one of Claims 20 to 32 wh rein the said at least one polymer used has a weight average molecular weight of from 5000 to 500,000.

34. A composition according to any one of Claims 20 to 34 wherein said composition comprises said at lest one polymer dispersed or dissolved in an aqueous- or organic-based carrier, vehicle, or medium therefor.

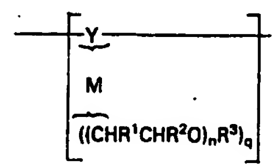
35. A composition according to Claim 34 wherein said composition comprises said at least one polymer dispersed or dissolved in an aqueous-based latex of a film-forming polymer or a paint made therefrom.

36. A composition according to any one of Claims 20 to 33 wherein said composition comprises said at least one polymer dispersed in a solid polymeric matrix.

37. A polymer having utility in the treatment of a surface of an object as to inhibit the adhesion of live organisms thereto, which polymer comprises



and one or more repeating units of general structure B



wherein X, which in the repeating units of structure A may be the same or different and Y, which in the repeating units of structure B may be the same or different, are hydrocarbyl residues or suitably substituted derivatives thereof;

Z, where present, which in the repeating units of structure A may be the same or different, is a group bearing a basic or an acidic substituent other than a carboxyl group;

R^1, which in the same repeating unit of Structure B (when n or q is two or more) or in different units of structure B may be the same or different, is hydrogen or methyl;

R^2, which in the same repeating unit of structure B (when n or q is 2 or more) or in different units of structure B may be the same or different, is hydrogen or methyl; except that

R^1 and R^2 in a single unit (CHR^1CHR^2O) cannot both be methyl;

R^3, which in the same repeating unit of structure B (when q is 2 or more) or in different repeating units of structure B may be the same or different, is hydrogen or a lower alkyl group containing up to five carbon atoms, or an acyl group derived from an alkanoic acid having up to five carbon atoms;

n is a number between 1 and 60;

p is 0, or a number of from 1 to 4;

q is a number of from 1 to 4.

38. A polymer according to Claim 37 wherein Z (where present) is a tertiary amino group.

39. A polymer according to Claim 38 wherein the units of structure are derived from the polymerisation of N,N-dimethyl-2-aminoethyl methacrylate.

40. A polymer according to any one of Claims 37 to 39 having the limitations of the said at least one polymer employed in the method according to any one Claims 2 to 5 and 10 to 14.

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